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^{13}C-Selective Infrared Multiple Photon Decomposition of *β*-Propiolactone, *β*-Butyrolactone, and Diketene with a CO_2 TEA Laser

Kyoko Sugita, Yoshiki Miyamoto, and Shigeyoshi Arai
Hill Research Co. Ltd., Roppongi 4-1-6, Minato-ku, Tokyo 106-0032, Japan

Shizuma Kuribayashi
Mitsubishi Heavy Industries, Sachiura 1-8-1, Kanazawa-ku, Yokohama 236-8515, Japan

Tetsuro Majima*
Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

Shunzo Yamamoto
Department of Chemistry, Faculty of Science, Okayama University, Tsushimanaka, Okayama, 700-8530, Japan

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^{13}C-Selective infrared multiple photon decomposition of lactone compounds has been studied using a CO_2 TEA (transversely excited atmospheric) laser. The main decomposition products were ethylene and CO_2 in *β*-propiolactone. We obtained CO_2 with a ^{13}C atomic fraction of 55% in the irradiation of 2 Torr (1 Torr = 1 mmHg = 133.322 Pa) *β*-propiolactone at 1035.47 cm^{-1}. The addition of 100 Torr of N_2 to 2 Torr of *β*-propiolactone resulted in a remarkable increase in selectivity, i.e., 75% ^{13}C in CO_2, while the yield was considerably decreased. Respective olefinic products were propylene and allene in the multiple photon decompositions of *β*-butyrolactone and diketene. The common product CO_2 was also found to be significantly enriched with ^{13}C in these lactone compounds.

Introduction

A number of papers have been published on laser isotope separation based on infrared multiple photon decomposition (IRMPD) of organic and inorganic compounds (see reviews).[1,2] In particular, the separation of ^{13}C by IRMPD has been studied most extensively because of the usefulness of the isotope in many research fields, especially in medical science. Large-scale laser separation of ^{13}C has been carried out by means of high repetition lasers,[3] multiple-frequency laser irradiation,[4] two-stage laser processes,[5−10] and refocusing multipasses.[11,12]

In most of these studies, the ^{13}C-selective IRMPD of difluorochloromethane ($CHClF_2$) induced by a CO_2 TEA laser is the fundamental photochemical process for the practical separation, because the compound exhibits excellent selectivity.[13] However, the ^{13}C-selective IRMPD under the optimum separation condition seems to require relatively high laser fluences.

Our previous study has demonstrated that *β*-propiolactone decomposes at low fluences below 1 J cm^{-2} in the CO_2 laser irradiation with the 9R(20) line at 1078.59 cm^{-1}.[14] Furthermore, our recent study has shown that the multiple photon excitation of the C=O stretching vibration mode by free electron laser pulses in a vicinity of 5.60 μm (1786 cm^{-1}) leads to the ^{13}C-selective IRMPD of *β*-propiolactone.[15] In the present paper, therefore, we re-examined the selectivity on ^{13}C in the IRMPD of *β*-propiolactone, *β*-butyrolactone, and diketene using CO_2 TEA laser lines in a wide wavenumber region. Although these compounds have many carbon atoms in each molecule, the CO_2 produced has considerably high fractions of ^{13}C.

Experimental Section

Experimental apparatus and procedures are essentially the same as those described in previous papers.[14,16] The irradiation cell was a cylindrical Pyrex tube with NaCl disk windows at both ends (length, 65 cm; volume, 220 mL). The beam from a Lumonics 103 TEA CO_2 laser was first truncated with a circular iris (diameter, 2.0 cm) and focused into a center of the irradiation cell by an infrared lens with a focal length of 80 cm. The pulse energy was adjusted adequately by inserting several sheets of polyethylene films into the laser beam. The CO_2 TEA laser was operated at a repetition rate of 0.5 Hz using the N_2-free lasing medium, i.e., the mixture of He and CO_2.

Amounts of products and isotope compositions were determined in the gas chromatograph mass spectrometry using a 3 m Gasukuropack (Gasukuro Kogyo) column. The column temperature was changed from room temperature to 150 °C for *β*-propiolactone, 180 °C for *β*-butyrolactone, and 200 °C in diketene at a rate of 4 °C per minute after keeping it at room temperature for several minutes. The CO_2 signal was corrected by subtracting the background signal in the gas chromatograph mass spectrometry.

Lactone compounds were obtained from Tokyo Kasei Co. and purified in vacuo by trap-to-trap distillation before use. Furthermore, CO_2 was completely removed from samples by evacuation at the temperature of dry ice. It is worthy noting

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* To whom correspondence should be addressed. Phone: 81-6-6879-8496. Fax: 81-6-6879-8499. E-mail: majima@sanken.osaka-u.ac.jp.

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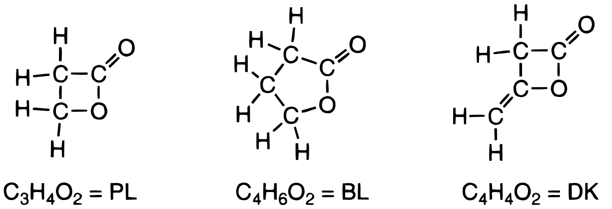

Figure 1. Structures of β-propiolactone (PL), β-butyrolacton (BL), and diketene (DK).

that vapor pressures of lactone compounds are relatively low, i.e., below a few Torr (1 Torr = 1 mmHg = 133.322 Pa) at room temperature. Preliminary gas chromatographic analyses showed that β-propiolactone, β-butyrolactone, and diketene contained a small amount of acetone as a common impurity. However, acetone does not have an intense infrared absorption band in the wavelength region used in the present IRMPD study. Diketene had several minor impurities in the gas-chromatographic analysis, after the trap-to-trap distillation was carried out. However, the impurities probably have almost no effect on the multiple photon absorption and following molecular decomposition processes, because absorption bands due to the impurities were not observed in the wavelength region used here for the IRMPD of diketene at the low pressures.

Results

Infrared absorption spectra for β-propiolactone (PL), β-butyrolacton (BL), and diketene (DK) are available in the previous paper[17] and spectroscopic data files.[18] The structures are presented in Figure 1. Generally speaking, lactone compounds (PL and BL) have intense absorption bands due to the stretching vibration mode of the C=O bond in the vicinity of 1800 cm^{-1}, and other intense bands assignable to the stretching vibration mode of either or both of (CO)−O and C−O in the lactone ring in the vicinity of 1100 cm^{-1}. For example, PL has intense absorption bands at about 930, 1100, and 1880 cm^{-1} and weak ones at about 1200, 1320, and 1430 cm^{-1}, where the carbonyl vibration mode corresponds to the band at 1880 cm^{-1} and the (CO)−O or C−O vibration mode does to the band at around 1100 cm^{-1}. The latter band of DK apparently shifts to a longer wavelength side (in the vicinity of 1010 cm^{-1}). Fortunately the red sides of these bands, where molecules containing ^{13}C can absorb multiple laser photons, fall within the tunable region of a CO_2 TEA laser.

The IRMPD of PL was found to produce CO_2 considerably enriched with ^{13}C, together with C_2H_4 in the irradiation with laser pulses in the appropriate wavenumber region from 1030 to 1060 cm^{-1}, as shown in Figure 2, where fluences at the beam waist have been adjusted within 1−2 J cm^{-2}. In the present experiment the selectivity β_{13} is defined as the ratio of ^{13}C to ^{12}C in the product divided by the ratio of ^{13}C to ^{12}C in the reactant. If the product is CO_2, the ratio in the reactant corresponds to 1.1/98.9. If the products are ethylene and propylene or allene, the ratios in the reactants closely equal 2.2/97.8 and 3.3/96.7, respectively. The 9P(32) line at 1035.47 cm^{-1} appears to give the maximum selectivity for ^{13}C of CO_2 in the IRMPD of PL. The fluence effects on selectivity and yield are presented in Figure 3, where the laser wavenumber is 1035.47 cm^{-1} and the pressure of PL is always 2 Torr. The selectivity β_{13} increases and the yield decreases rapidly with decreasing fluence. The addition of 100 Torr of N_2 to 2 Torr PL resulted in the remarkable increase in the selectivity β_{13} of ^{13}C, producing CO_2 with ^{13}C atom in fractions higher than 70%, although the yield per pulse decreased by a factor of 30 (see Table 1). In contrast, we did not observe any meaningful enrichment of ^{13}C in C_2H_4 produced from the IRMPD at various wavenumbers.

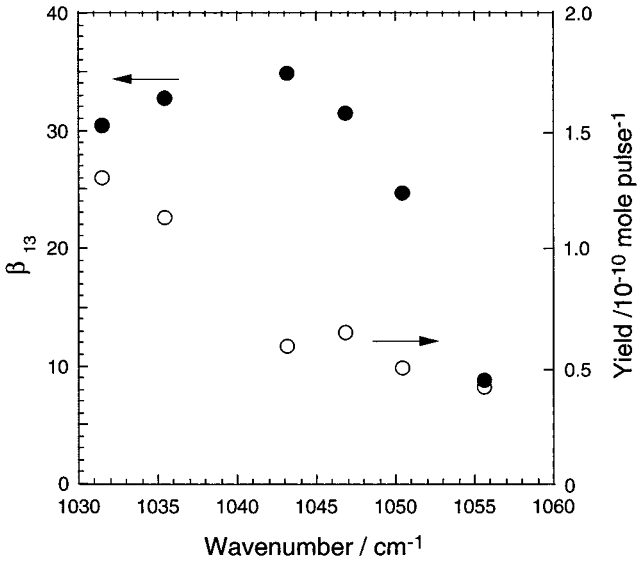

Figure 2. Wavenumber dependences of product yields and selectivity β_{13} in ^{13}C-selective IRMPD of 1 Torr β-propiolactone. Fluences at a beam waist are in the region between 1.0 and 2.0 J cm^{-2}. (circles) Yields of CO_2 per pulse; (solid circles) selectivities of ^{13}C in CO_2.

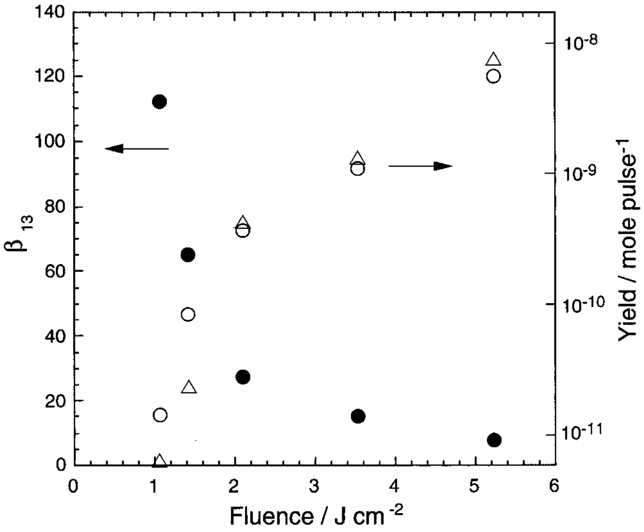

Figure 3. Fluence dependences of product yields and selectivity β_{13} in ^{13}C-selective IRMPD of 2 Torr β-propiolactone. The wavenumber of laser pulses is 1035.47 cm^{-1}. (circles) Yields of CO_2 per pulse; (triangles) yields of C_2H_4 per pulse; (solid circles) selectivities of ^{13}C in CO_2.

TABLE 1: Effect of N_2 on ^{13}C-Selective IRMPD of 2 Torr β-Propiolactone[a]

pressure Torr	number of pulses	total amounts of CO_2 10^{-8} mol	selectivity β_{13}[b]
0	500	24	27
100	1000	1.5	250
100	3000	4.9	290

[a] Laser line, 9P(32) at 1035.47 cm^{-1}; fluence at a beam waist, about 2 J cm^{-2}. [b] Ratio of ^{13}C to ^{12}C in product CO_2 divided by ratio of ^{13}C to ^{12}C in reactant.

Figure 4 presents isotope selectivity β_{13} on ^{13}C in CO_2, and yields of CO_2 and propylene (C_3H_6) per pulse as a function of laser line in the ^{13}C-selective IRMPD of 1 Torr BL, where a CO_2 laser itself does not have lines between 1060 and 1065 cm^{-1}. There seems to be the maximum selectivity in the vicinity

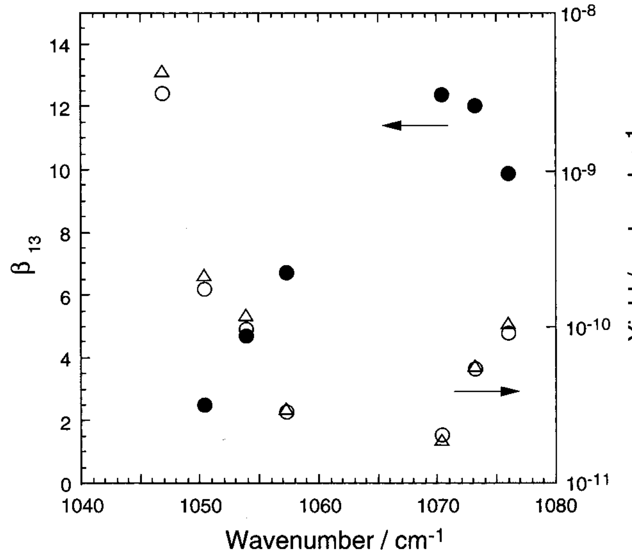

Figure 4. Wavenumber dependences of product yields and selectivity β_{13} in ^{13}C-selective IRMPD of 1 Torr β-butyrolactone. Fluences at a beam waist are in the region between 0.8 and 1.1 J cm^{-2}. (circles) yields of CO$_2$ per pulse; (triangles) yields of C$_3$H$_6$ per pulse; (solid circles) selectivities of ^{13}C in CO$_2$.

TABLE 2: ^{13}C-Selective IRMPD of 2 Torr Diketene

laser		selectivity β_{13}		yield[a]	
wavelength cm^{-1}	fluence[b] J cm^{-2}	^{13}C in CO$_2$[c]	^{13}C in C$_3$H$_4$[d]	CO$_2$ 10^{-11} mol	C$_3$H$_4$ 10^{-11} mol
936.8	4.0	3.7	3.1	3.3	
944.2	4.4	2.5	2.5	13	9.6
946.0	4.2	6.0	2.4	40	28
947.7	4.4	25	4.0	37	39
949.5	3.7	19	3.4	41	47
951.2	4.4	13	2.1	63	71
952.9	3.7	14	2.2	41	41
966.3	3.6	4	3.9	270	330

[a] Yields of CO$_2$ and C$_3$H$_4$ (allene) per pulse. [b] Fluence at a beam waist. [c] Ratio of ^{13}C to ^{12}C in product CO$_2$ divided by ratio of ^{13}C to ^{12}C (1.1/98.9) in reactant. [d] Ratio of ^{13}C-containing allene to ^{12}C allene divided by ratio of ^{13}C to ^{12}C (3.2/96.7) in reactant.

of 1070 cm^{-1}, the wavenumber of which corresponds to a lower energy side of the intense band with a peak at about 1120 cm^{-1}. The band may be caused by the (CO)−O bond. BL has the intense infrared band with a peak at 1020 cm^{-1}; the corresponding band is absent in the infrared spectrum of PL. The decomposition yield apparently has the minimum between the two at 1020 and 1120 cm^{-1}. We did not observe the ^{13}C enrichment in the hydrocarbon product C$_3$H$_6$; the selectivity is nearly 1.

Table 2 tabulates selectivities and yields of CO$_2$ and C$_3$H$_4$ (allene) in the ^{13}C-selective IRMPD of 2 Torr DK. Laser pulses in the vicinity of 950 cm^{-1} show high selectivity on ^{13}C of CO$_2$. In contrast with PL and BL, the hydrocarbon product C$_3$H$_4$ appears to be enriched with ^{13}C to a meaningful extent. The decrease in fluence did not change the selectivity β_{13} on ^{13}C in CO$_2$ in the IRMPD of DK.

Discussion

Yamamoto and co-workers have studied mercury-photosensitized, cadmium-photosensitized, thermal, and infrared multiple photon decompositions of various lactone compounds in the gas phase.[14,15,19−22] It is possible for PL to undergo the following ring cleavages in highly and vibrationally excited states.

β-propiolactone (C$_3$H$_4$O$_2$ = PL)

$$\rightarrow \mathrm{C_2H_4} + \mathrm{CO_2} \qquad \Delta H = -10.7\ \mathrm{kJ\ mol^{-1}} \tag{1}$$

$$\rightarrow \mathrm{CH_3CHO} + \mathrm{CO} \qquad \Delta H = 54.2\ \mathrm{kJ\ mol^{-1}} \tag{2}$$

$$\rightarrow \mathrm{CH_2CO} + \mathrm{H_2CO} \qquad \Delta H = 153.6\ \mathrm{kJ\ mol^{-1}} \tag{3}$$

The activation energy for reaction 1 has been found to be 191.7 or 180.5 kJ mol^{-1} in pyrolysis studies on PL.[23,24] Considering from enthalpy changes, reactions 2 and 3 are presumed to have much higher activation energies than reaction 1, and therefore, do not occur appreciably at low fluences examined in this experiment.

It is also possible for PL to undergo the following isomerization:

$$\beta\text{-propiolactone (PL)} \rightarrow \text{acrylic acid } (\mathrm{CH_2CHCOOH}) \tag{4}$$

The isomerization is estimated to be exothermic by 10−20 kJ mol^{-1}, where the heat of formation for liquid acylic acid is 383.8 kJ mol^{-1} and the ΔH (liquid acylic acid → gas acylic acid) is assumed to be = 30−40 kJ mol^{-1}. However, the observed material balance has shown that more than 90% of PL is converted into C$_2$H$_4$ and CO$_2$ in the irradiation of 2.5 Torr β-propiolactone with 400 laser pulses at a fluence of 0.66 J cm^{-2}, where the wavenumber of the laser is 1078.59 cm^{-1}.[14] The previous result means that the isomerization of PL does not occur appreciably, although the laser line used differs from those in the present study. Frey and Pidgeon have reported that the isomerization is the minor and heterogeneous process in the thermal decomposition of PL.[24] Similarly to PL, BL and DK decompose mainly into olefins and CO$_2$ in the IRMPD.

β-butyrolactone (C$_4$H$_6$O$_2$ = BL)

$$\rightarrow \text{propylene } (\mathrm{C_3H_6}) + \mathrm{CO_2} \tag{5}$$

$$\text{diketene } (\mathrm{C_4H_4O_2} = \mathrm{DK}) \rightarrow \text{allene } (\mathrm{C_3H_4}) + \mathrm{CO_2} \tag{6}$$

The fact that the yields of CO$_2$ are nearly the same as propylene and allene supports the decomposition reactions 5 and 6. There were no peaks due to decomposition products other than CO$_2$ and corresponding olefins in the gas chromatograms for fluences used here.

We did not observe meaningful enrichment of ^{13}C in ethylene and propylene for the respective IRMPD of PL and BL, although CO$_2$ showed high atomic fractions of ^{13}C. Therefore, the laser radiation may be absorbed by the bands due to the stretching vibration of the (CO)−O bond rather than the (CH$_2$)−O or (CH$_3$-CH)−O bond in PL and BL, although both bands may be located closely in infrared spectra for PL and BL. In the IRMPD of DK, however, C$_3$H$_4$ appears to be enriched to a meaningful extent with ^{13}C, as tabulated in Table 2. We consider that the stretching vibration modes of both (CO)−O and (CH$_2$C)−O bonds are resonant with the laser light in DK.

The TEA CO$_2$ laser has been operated in the present experiment using only helium and CO$_2$ as the lasing medium; the pulse profile has a fwhm of about 80 ns without a tail. However, collisional processes probably contribute somewhat to the excitation of PL at 2 Torr. Highly excited molecules in the vibrational modes, which decompose into ethylene and CO$_2$, may be produced from direct multiple-photon absorption as well as collision-assisted excitation followed by further multiple-photon excitation. The former excitation shows higher isotope selectivity as compared to the latter collision-assisted excitation under the present irradiation condition. Nitrogen molecules may quench more efficiently the latter process, which is slower than the direct optical excitation. The quenching of collision-assisted excitation can explain the large increase in selectivity on ^{13}C and also the large decrease in the yield of decomposition observed for the addition of nitrogen to PL.

When the fluence necessary for the occurrence of IRMPD is higher, the laser beam must be more tightly focused into a small area with a lens. As the result, only a limited number of molecules are illuminated with laser beams and the yield of the decomposition cannot be high in such a tight optical geometry. $CHClF_2$ undergoes ^{13}C-selective IRMPD at fluences larger than about 3 J cm^{-2} using laser pulses in the vicinity of 1040 cm^{-1}. This disadvantage is overcompensated by the higher pressure without the ^{13}C-selectivity breakdown in ^{13}C-selective IRMPD of $CHClF_2$.[11-13]

On the other hand, PL decomposes at fluences below 1 J cm^{-2}, which are obtainable with a high-power TEA CO_2 laser without focusing the beam. Since PL has nine atoms in a molecule, vibrational levels are placed densely along the excitation ladder. The high density makes the multiple-photon absorption relatively efficient at fluences as low as 1 J cm^{-2}. In addition, reactions 1 and 5 have activation energies of 180−190 and 163 kJ mol^{-1}, respectively,[23-25] while the activation energy for the decomposition of $CHClF_2$ into CF_2 and HCl has been reported to be 230 kJ mol^{-1}.[26] The low activation energy is favorable to occurrence of the IRMPD of PL and BL. Recently, we have found that $CHBrF_2$ is an efficient working molecule for ^{13}C enrichment by IRMPD as well as $CHClF_2$.[27] However, lactone compounds are also promising, if they are usable in other chemical industries after isotope separation. The enrichment of ^{13}C in the product means the depletion of the same isotope in the original material, so that one can obtain pure $^{12}CO_2$ in the pyrolysis of the parent lactone after the extensive IRMPD.

Concluding Remarks

In the ^{13}C-selective IRMPD of large molecules containing more than two carbon atoms, one cannot easily attain the high enrichment of ^{13}C with a high yield. However, the molecule with a nonequivalent carbon atom such as lactone enables us to attain the high enrichment, if the multiple photon absorption relating the key atom occurs and the following decomposition gives the C1 product involving the key atom. We successfully obtained CO_2 with ^{13}C at more than 50% in the IRMPD of pure β-propiolactone, where CO_2 and C_2H_4 were the observed products. The addition of nitrogen to β-propiolactone increased selectivities above 70%, although corresponding yields were decreased considerably. ^{13}C-selective IRMPD has been also observed for β-butyrolactone and diketene.

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References and Notes

(1) Letokhov, V. S. *Nonlinear Laser Chemistry*; Springer Ser. Chem. Phys. 22; Springer-Verlag: Berlin, 1983.

(2) Oyama, T.; Arai, S. *Rev. Laser Eng.* **1982**, *10*, 193. Arai, S.; Ishikawa, Y.; Oyama, T.; Arai, S. *Rev. Laser Eng.* **1985**, *13*, 707.

(3) Baranov, V. Yu. *IEEE J. Quantum Electron.* **1983**, *QE−19*, 1577.

(4) Evseev, A. V.; Letokov, V. S.; Puretzky, A. A. *Appl. Phys.* **1985**, *B36*, 93.

(5) Gautheir, M.; Cureton, C. G.; Hackett, P. A.; Willis, C. *Appl. Phys.* **1982**, *B28*, 43.

(6) Arai, S.; Sugita, K.; Ma, P. H.; Ishikawa, Y.; Kaetsu, H.; Isomura, S. *Chem. Phys. Lett.* **1988**, *151*, 516.

(7) Arai, S.; Sugita, K.; Ma, P. H.; Ishikawa, Y.; Kaetsu, H.; Isomura, S. *Appl. Phys.* **1989**, *B48*, 427.

(8) Sugita, K.; Ma, P. H.; Ishikawa, Y.; Arai, S. *Appl. Phys.* **1991**, *B52*, 266.

(9) Parthasarathy, V.; Sarkar, S. K.; Iyer, N. V.; Rama Rao, K. V. S.; Mittal, J. P. *Appl. Phys.* **1993**, *B56*, 321.

(10) Batra, A.; Sarkar, S. K.; Parthasarathy, V. *J. Photochem. Photobiol.* **1994**, *A83*, 193.

(11) Fuss, W. Gothel, J.; Ivanenko, M. M.; Kompa, K. L.; Schmid, W. E.; Witte, K. *Z. Phys*. **1994**, *D29*, 291.

(12) Gothel, J.; Ivanenko, M.; Hering, P.; Fuss, W.; Kompa, K. L. *Appl. Phys*. **1996**, *B62*, 329.

(13) Fuss, W. Gothel, J.; Ivanenko, M. M.; Schmid, W. E.; Hering, P.; Kompa, K. L.; Witte, K. *Isotopenpraxis Environ. Health Stud*. **1994**, *30*, 199.

(14) Yamamoto, S.; Ishikawa, Y.; Arai, S. *Bull. Chem. Soc. Jpn*. **1986**, *59*, 2241.

(15) Kuribayashi, S.; Zako, A.; Matsumoto, Y.; Yamamoto, S.; Arai, S. *Nucl. Instrum. Methods B*, submitted.

(16) Sugita, K.; Majima, T.; Arai, S. *J. Phys. Chem. A* **1999**, *103*, 4144.

(17) During, J. R. *Spectrochem. Acta* **1963**, *19*, 1225.

(18) For example: *The Aldrich IR Library*; Aldrich Chemical Co.: Milwaukee.

(19) Yamamoto, S.; Matsuda, S.; Ozaki, C.; Takahoso, H.; Nishimura, N. *Bull. Chem. Soc. Jpn*. **1984**, *57*, 3408.

(20) Yamamoto, S.; Takahoso, H.; Sueishi, Y.; Nishimura, N. *Bull. Chem. Soc. Jpn*. **1985**, *58*, 2038.

(21) Yamamoto, S.; Gohda, R.; Sueishi, Y.; Nishimura, N. *Bull. Chem. Soc. Jpn*. **1989**, *62*, 2235.

(22) Yamamoto, S.; Suzuki, M.; Sueishi, Y.; Nishimura, N.; Ishikawa, Y.; Arai, S. *Bull. Chem. Soc. Jpn*. **1992**, *65*, 3112.

(23) James, T. L.; Wellington, C. A. *J. Am. Chem. Soc*. **1969**, *91*, 1969.

(24) Frey, H. M.; Pidgeon, I. M. *J. Chem. Soc. Faraday Trans. 1* **1985**, *81*, 1087.

(25) Frey, H. M.; Watts, H. P. *J. Chem. Soc. Faraday Trans. 1* **1983**, *79*, 1659.

(26) Barnes, G. R.; Cox, R. A.; Symons, R. F. *J. Chem. Soc. B* **1971**, 1176.

(27) Arai, S.; Ikawa, K.; Matsumoto, Y.; Iizuka, Y.; Sugita, K.; Sarkar, S. K.; Kuribayashi, S. *Nucl. Instrum. Methods, Phys. Res. B* **1998**, *B144*, 193.